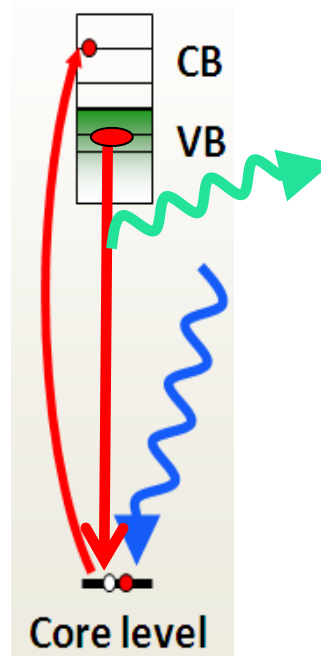
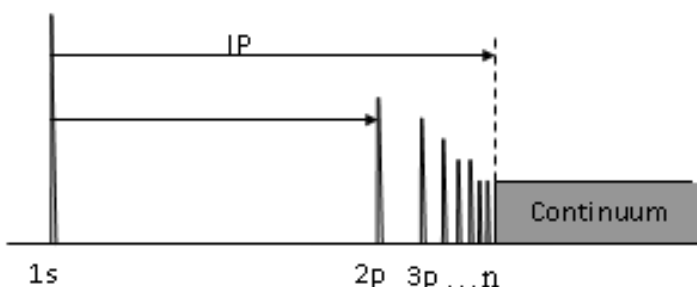


X-ray absorption techniques (XAS = NEXAFS = XANES)

The technique of x-ray absorption spectroscopy (XAS) also known as NEXAFS (near edge X-ray absorption fine structure), emerged with the availability of tunable photon sources, i.e., synchrotron radiation facilities, particularly in the soft-X-ray range. The first NEXAFS spectrum of an adsorbed molecule, CO on Ni(100) was reported in 1981 by J. Stöhr, K. Baberschke, R. Jaeger, T. Treichler and S. Brennan, in Phys. Rev. Letters, 47, 381. Sometimes it is also called XANES (X-ray absorption near edge structure). In XAS one measures the absorption of photons as the energy is scanned across a core ionization threshold.

The threshold of absorption occurs when $h\nu$ matches the binding energy (relative to the Fermi level of the sample) of a core level. The absorption probability is then proportional to the density of empty states in the final state $\langle f |$



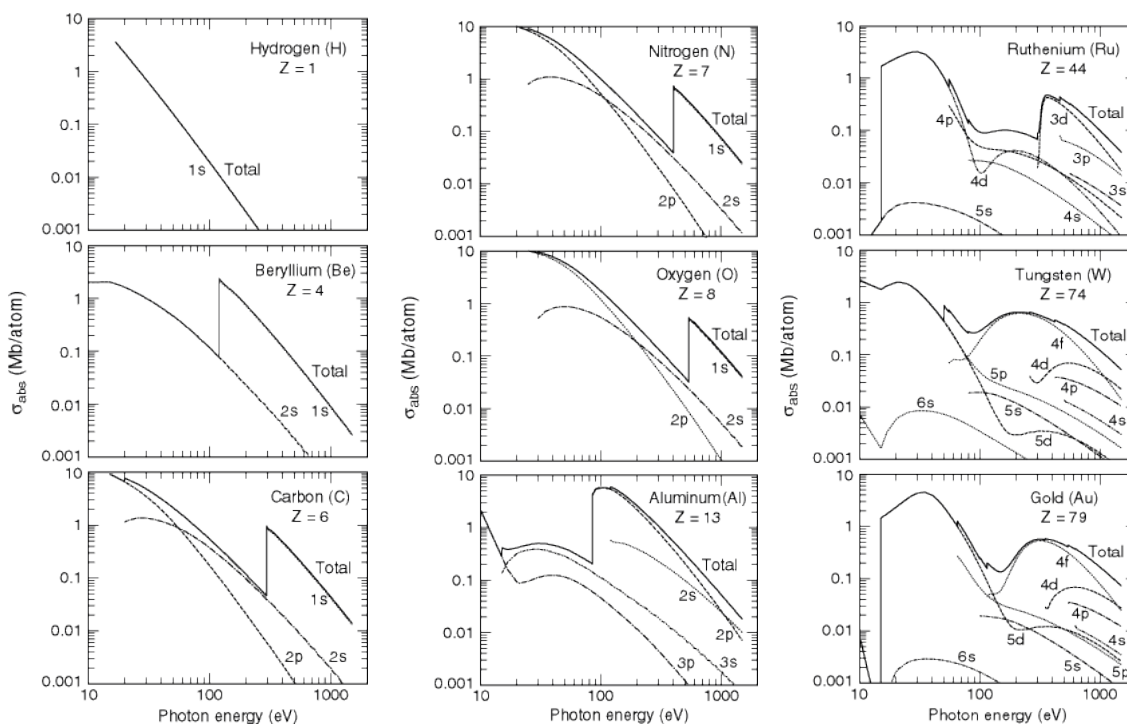
The empty states however, are not those of the ground state molecule, but those of the molecule with a core hole. It is clear then that the measured density is a perturbed one. The spectrum contains the so-called Rydberg resonances, corresponding to the hydrogenic states of the ionized core. The absorption peaks are spaced closer to each other as they approach the vacuum level energy which corresponds to photons with energy equal to the ionization potential, IP. The final state corresponds to a hole in the inner core level and an additional electron in a previously empty state. Obviously the remaining electrons rearrange due to the presence of the hole (for ionization) plus the extra electron. One approximation, the Koopman's theorem, states that $IP = E_{\text{binding}}$, i.e., it assumes that after removing the electron from the s-level, the others remain frozen in their states. This assumption leads to errors of up to several eV's, particularly for the light elements. The relaxation energy due to the rearrangement of the remaining electrons can be calculated or approximated in several ways. One is the equivalent cores approximation, which assumes that the outer electron states are perturbed as if the nuclear charge was increased by one, i.e., they are the same as the next element in the periodic table.

The x-ray absorption can be measured directly in transmission, or indirectly by measuring the decay products of the core hole. For example the fluorescence emission. The fluorescent photons come from the radiative recombination of the initial core hole. One can also measure the emitted electrons, for example the Auger electrons from the

core hole, or the secondary low energy electrons. This is called the electron yield mode, Auger or total yield. The advantage of electron yield is that the signal comes from the surface layers, which is important in surface science.

One advantage of NEXAFS is that it is element specific. For example by measuring the structure at the threshold of the O 1s level one is measuring the local electronic structure around the O atoms, which is dominated by the O molecular (empty) orbitals.

One important observation is the following: NEXAFS is useful only for those transitions that are sharp, which includes many of the core levels (K, L) of familiar elements like C, N, O, C, and many s-type orbitals of heavier elements. The first are accessible in soft x-ray synchrotrons ($E \sim \text{few } 100 \text{ eV}$), the later require hard x-rays ($h\nu \sim \text{several KeV}$). Good sharp edges are shown below (left and middle). Broad edges are shown on the right column.



From :

J.-J. Yeh and I. Lindau, "Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: $1 < Z < 103$," *At. Data Nucl. Data Tables* **32**, 1 (1985).

J.-J. Yeh, *Atomic Calculations of Photoionization Cross Sections and Asymmetry Parameters* (Gordon and Breach, Langhorne, PA, 1993).

Selection rules in photoelectron spectroscopy

In this section we discuss some important selection rules in photoelectron spectroscopy that are connected with the dipolar nature of the excitation, similar to the case of intra-atomic transitions where we have the well known dipolar selection rule: $\Delta l = \pm 1$ for the angular momentum quantum number.

The absorption probability per unit time can be calculated from the Golden Rule for the harmonic perturbation potential $V(t) = V_0 \cdot e^{-i\omega t}$:

$$P = \frac{2\pi}{\hbar} \left| \langle f | V | i \rangle \right|^2 \cdot \rho_f(E)$$

$\rho_f(E)$ is the final density of states for the energy $E = h\nu - E_i$. For our photon field, $V(t) = (e/mc) \cdot \mathbf{A} \cdot \mathbf{p}$, where \mathbf{A} is the electromagnetic vector potential and \mathbf{p} the linear momentum operator. Since the gauge relation between \mathbf{E} (electric field) and \mathbf{A} exists:

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

it is clear that \mathbf{A} and \mathbf{E} are parallel to each other: $\mathbf{A} = A_0 \cdot \cos(\mathbf{k} \cdot \mathbf{x} - \omega t)$; $\mathbf{E} = -\omega A_0 / c \cdot \sin(\mathbf{k} \cdot \mathbf{x} - \omega t) = \mathbf{E}_0 \cdot \sin(\mathbf{k} \cdot \mathbf{x} - \omega t)$

Expressing the cos or sin function in exponential form $(e^x + e^{-x})/2$ we get for the absorption probability:

$$P_{i,f} \propto \left| \langle f | e^{i\vec{k}\vec{x}} \cdot \vec{E}_0 \cdot \vec{p} | i \rangle \right|^2 \cdot \rho(E)$$

The dipolar approximation has the first term $e^{i\vec{k}\vec{x}} \approx 1$, when $\mathbf{k} \cdot \mathbf{x} \ll 1$. For photons of 280 eV (carbon K edge), $k = 0.51 \times 10^{-3} \times 280 = 0.14 \text{ \AA}^{-1}$, and $x \approx 2a_0/Z = 1/12 \text{ \AA}$ (the diameter of the C 1s “orbit”), so that $\mathbf{k} \cdot \mathbf{x} \approx 0.012$. So the approximation:

$$P_{i,f} \propto \left| \langle f | \vec{E}_0 \cdot \vec{p} | i \rangle \right|^2 \cdot \rho(E)$$

is sufficiently good for most practical cases. We already see that in order to have $P_{i,f} \neq 0$, one at least of the terms:

$$E_x \cdot \left\langle f \left| \frac{\partial}{\partial x} \right| i \right\rangle; \quad E_y \cdot \left\langle f \left| \frac{\partial}{\partial y} \right| i \right\rangle; \quad E_z \cdot \left\langle f \left| \frac{\partial}{\partial z} \right| i \right\rangle$$

must be different from 0. Because of the symmetry properties of the $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$ operators (they change sign upon reflections, inversions etc.), the symmetry of the initial and final states cannot be random.

Let us examine some consequences of the selection rules in photoemission spectroscopy. The final state is of course a free electron represented by a plane wave in the direction of the detector. Let's imagine the local group to be of the C_{2v} type, which means a binary rotation axis (the x-axis) and 2 reflection planes (x-z and y-z). The operators $\partial/\partial x, y, z$ belong respectively to the B_1, B_2 and A_1 representations ($\partial/\partial(-x) = -\partial/\partial x$; etc.). If the detector is pointing in the direction normal to the surface, it is clear that the final state is totally symmetric with respect to the operation of the C_{2v} group and therefore belongs to the A_1 representation. No emission can then be obtained from initial states belonging to the A_2 representation.

The polarization of the photon plays a crucial role. For p-polarized photons (electric field vector E in the plane of incidence) and x-z incidence plane $E_y = 0$, we can get no information about states of the B_2 type but we get emission from A_1 and B_1 type states. If in addition the angle of incidence is grazing, so that $E_x \sim 0$, ($E \parallel z$), then only emission from A_1 is obtained. For s-polarized light ($E \perp$ plane of incidence), we have $E_z = 0$ and only emission from B_1 and B_2 is obtained. If in addition the incidence plane coincides with the x-z or y-z plane, the emission is from pure B_2 or B_1 respectively. This reasoning gives the tone for an analysis of the photoemission spectrum in connection to surface symmetries, polarization effects and angle of incidence (photon) and emergence (photoelectron).

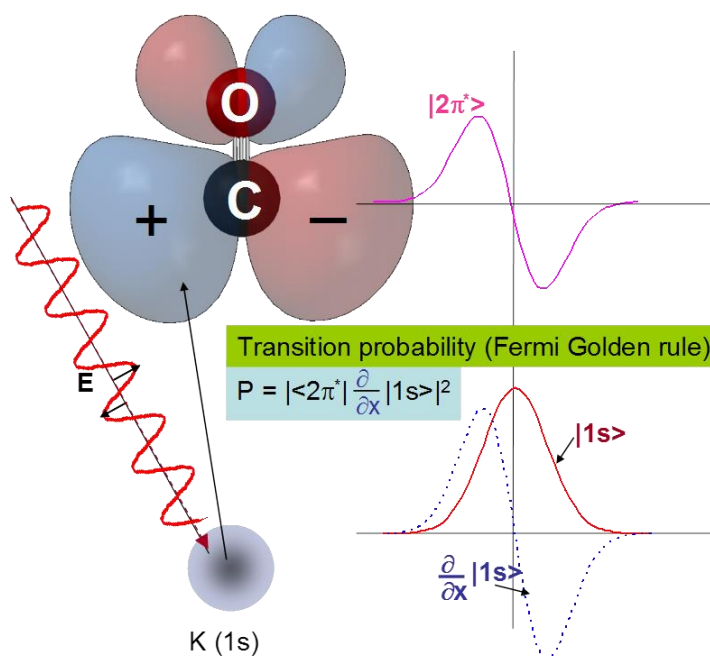
As an illustration of the application of the selection rules described above, let's consider the x-ray absorption by an electron in the $1s$ level of C in CO that is excited into an empty level of the $2\pi^*$ antibonding orbital, as illustrated in the figure below. If the polarization of the photon is such that the electric field has a component in the direction x , which we assume is perpendicular to the C-O bond, then the amplitude of the wavefunction in the final

state $|2\pi^*\rangle$ goes from + to - across the origin. The initial state $|C1s\rangle$ is symmetric. The operator $\partial/\partial x$ changes the wavefunction as shown below, i.e., it makes it antisymmetric.

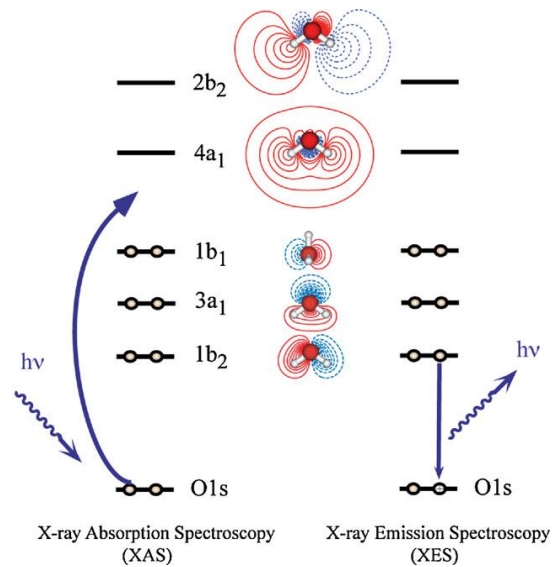
Therefore the product:

$$|\langle 2\pi^* | E \cdot \partial/\partial x | C1s \rangle| \neq 0$$

In the following pages we look at examples that illustrate the capabilities of NEXAFS.

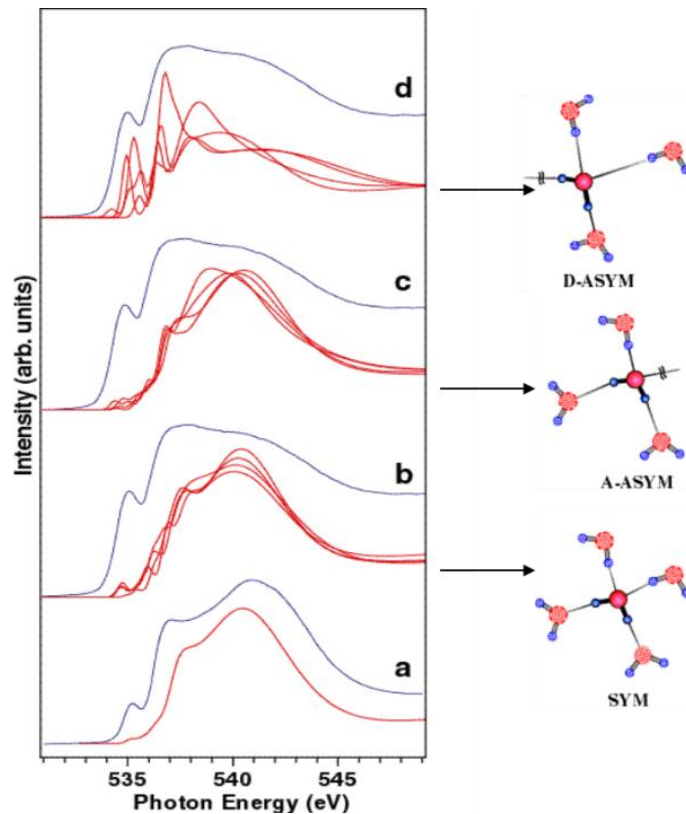


Example 1: The melting of ice



Theoretical NEXAFS spectra of water in various configurations (red curves) compared with experimental measurement (blue). On the right drawings of the water bonding configuration producing the red curves.

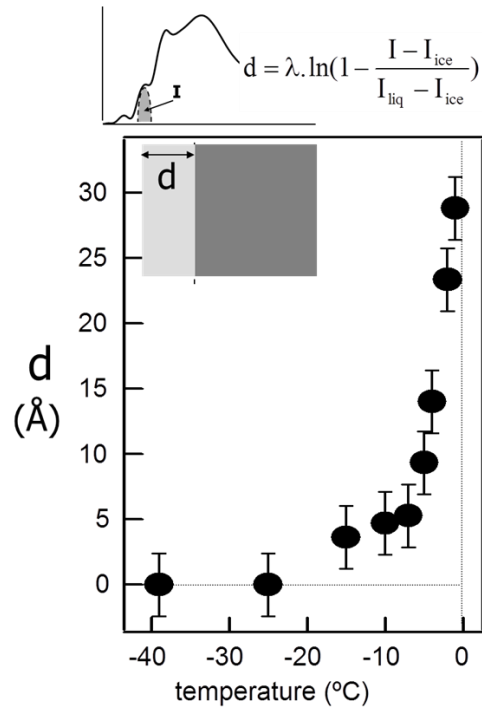
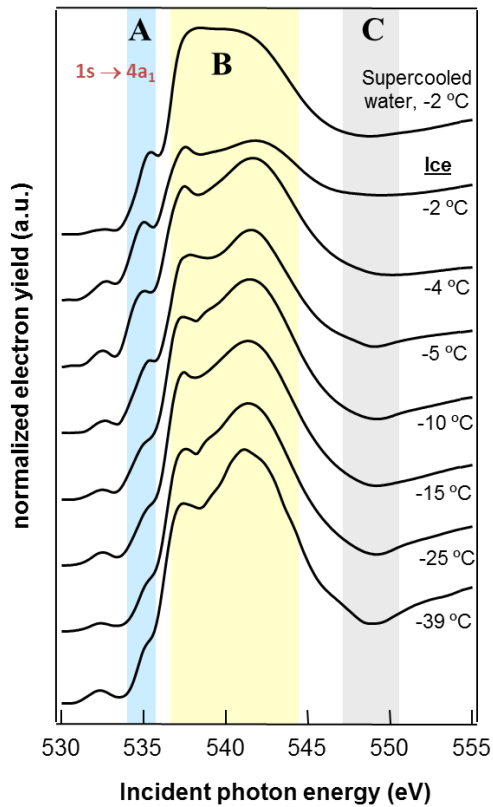
From S. Myneni, Y. Luo, L.Å. Näslund, M. Cavalleri, L. Ojamäe, H. Ogasawara, A. Pelmenchikov, Ph. Wernet, P. Väterlein, C. Heske, Z. Hussain, L.G.M. Pettersson, and A. Nilsson in J. Phys. Cond. Matt.



Experimental results:

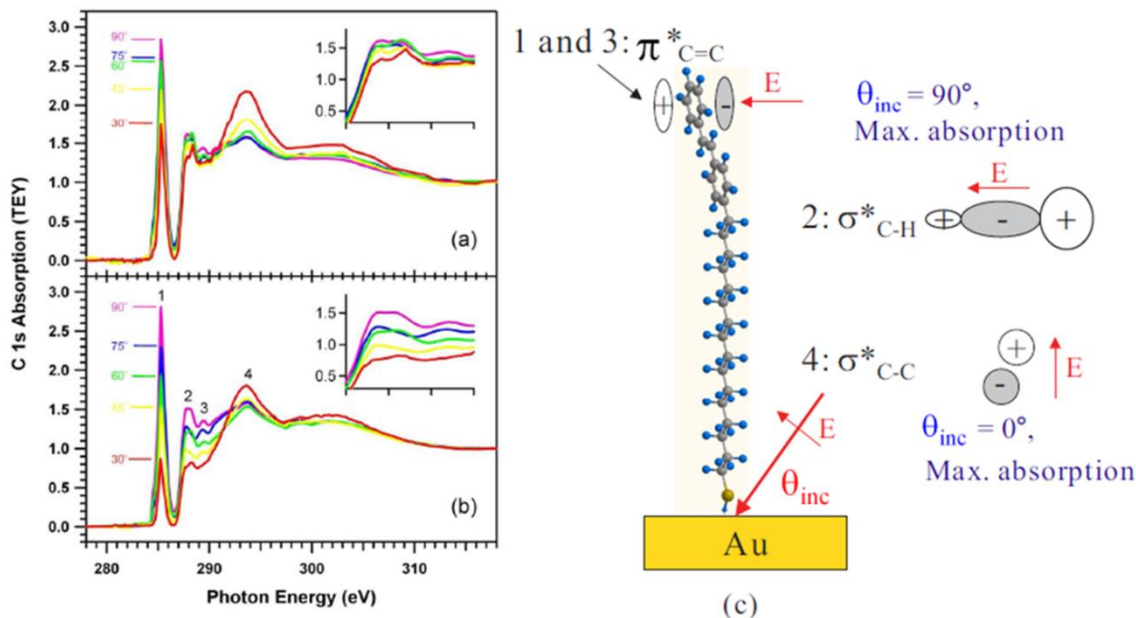
Ice was condensed on a Cu plate from its vapor. It was subsequently heated all the way to the melting point at 0° C while acquiring spectra in the electron yield mode to ensure surface sensitivity.

From: H. Bluhm, D.F. Ogletree, C.S. Fadley, Z. Hussain and M. Salmeron. J. Phys. Condens. Matt. 14, L227 (2002).



Example 2: Applications of NEXAFS to determine molecular orientation:

a) Transtilbene on Au(111)

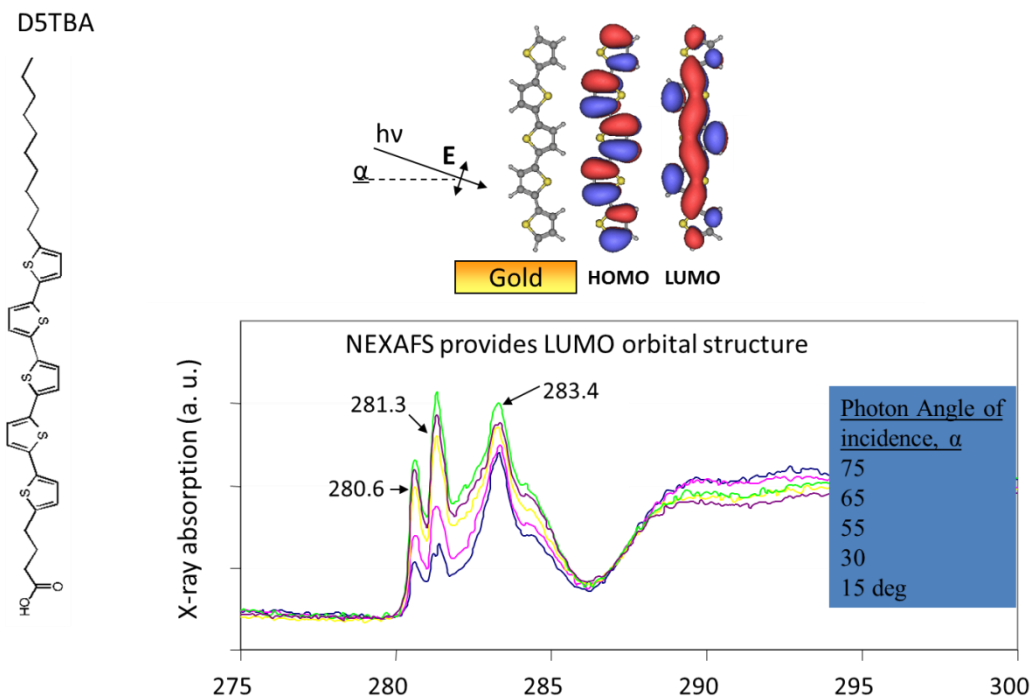


Notice the change in the intensity of the absorption peaks from the C1s core to various empty orbitals (LUMOs) depending on the symmetry of the final state relative to the photon electric field (E).

From the paper: *Influence of molecular ordering on electrical and friction properties of omega-(trans-4-stilbene) alkylthiol self-assembled monolayers on Au (111)*. Yabing Qi, et al.

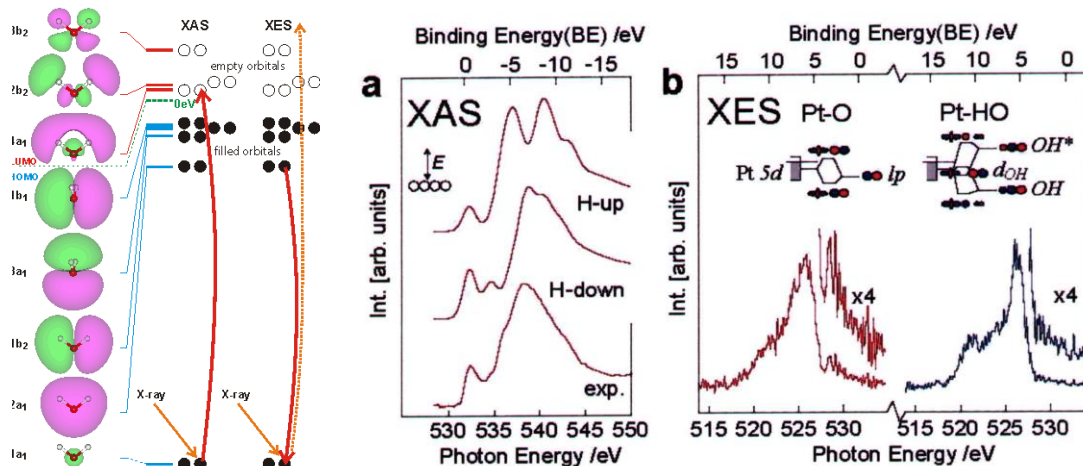
Langmuir, 26(21) 16522-6528 (2010)

b) Decyl-pentathiophene butiric acid (D5TBA) on Au(111)



X-ray emission (XES)

If one disperses the fluorescence photons emitted when the core hole is de-excited one obtains the x-ray emission spectrum or XES. To disperse the photons one typically uses a diffraction grating, similar to the one used to disperse the x-rays from the synchrotron ring before impinging on the sample. Like XAS, XES provides also a local



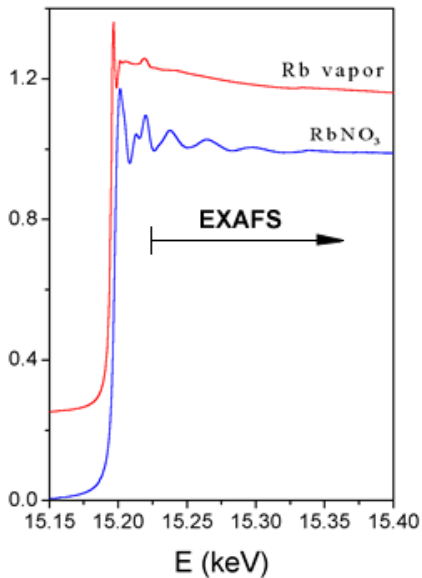
electronic structure around the emitting atom, except that now one obtains the occupied orbitals instead of the empty ones in XAS. So the two techniques are complementary. The illustration shows the two processes for the case of O 1s in water and its valence orbitals. The figure shows actual spectra from a water monolayer adsorbed on Pt(111).

XES contains similar information as photoelectron spectroscopy (XPS) where photons directly excite electrons from states in the conduction or valence bands. Like NXAFS however, the density of states (DOE) obtained is local, centered around the atom whose core hole is excited. This element sensitivity is exploited to discern contributions to the DOE from surface atoms or adsorbates, etc. If these elements were present in small concentration the DOE from XPS might not be able to show the extra peaks or changes in the DOE due to these minority species. The example shown above illustrates the case of water on Pt(111) where O is only a fraction of the surface atoms and XPS would be dominated by states due to the Pt atoms at the surface and several layers below it (within the electron mean free path).

Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS measurements involve scanning the photon energy around the absorption edges of the atoms in a material or on a surface. The fine structure in the absorption cross section gives information about the neighbors of the emitting atoms. The main advantages of these x-ray absorption techniques are that they work for materials where long-range order is not present and that at least the nearest neighbor distances can be obtained with rather high precision. The figure shows an X-ray absorption spectra of RbNO₃ water solution and rubidium vapor in the energy range of the Rb K-edge. Above the edge oscillations in the cross section are superimposed. These are the EXAFS oscillations. The physical origin of these oscillations is quite easy to understand.

The figures below are from: <http://www.p-ng.si/~arcon/xas/exafs/exafs.htm>



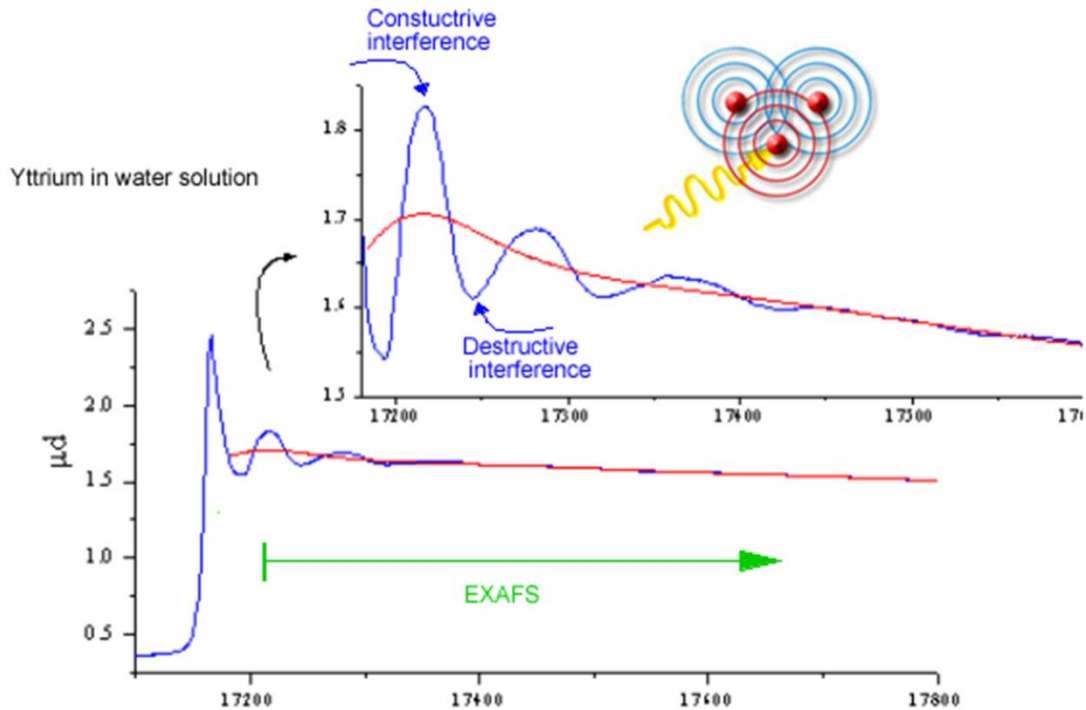
X-ray absorption spectra of RbNO₃ water solution and rubidium vapor in the energy range of Rb K-edge.

$$\chi = \sum_{\text{shells}} n_X \cdot S_0^2 \cdot \frac{f_X(k)}{k \cdot r^2} e^{-2k^2 \sigma^2} \sin(2kr + \alpha_{MX}(k))$$

n_X = # of X atoms in shell
 S_0^2 = amplitude reduction factor
 $f_X(k)$ = amplitude function
 $k \cdot r^2$ = amplitude reduction factor
 $e^{-2k^2 \sigma^2}$ = Debye-Waller term
 $\sigma^2 = \sigma_{\text{stat}}^2 + \sigma_{\text{vib}}^2$
 $\sigma < 0.10 \text{ \AA}$
 $\sin(2kr + \alpha_{MX}(k))$ = phase function
 r = (average) MX distance

The absorption cross section is given by Fermi's golden rule $\rightarrow \langle f | H | i \rangle$, with the initial state being the localized core state. The final state is an outgoing electron wave that contains all the multiple scattering processes. The oscillations due to the scattered waves from the neighbors added coherently to the outgoing wave. This gives a periodicity determined by the nearest neighbor distance. This simple picture works only for electron energies which are not too close to the edge. Below kinetic energies of 50eV or so the oscillations contain resonant absorption from the valence states.

Schematics of the EXAFS process illustrating the origin of EXAFS oscillations due to the interference of outgoing and backscattered photoelectron wave.



It is convenient to extract the EXAFS oscillations from the slowly varying background. This is done by the definition of a “fine structure function” χ :

$$\chi(k) = \frac{\sigma(k) - \sigma_0(k)}{\sigma_0(k)}$$

σ is the measured absorption and σ_0 is the absorption due to the free atom. If we consider a simple single-scattering picture the fine structure function is given by:

$$\chi(k) = -k^{-1} \sum A_i(k) \sin [2kR_i + \phi_i(180^\circ, k)]$$

where k is the electron wave number, A_i the amplitude function and ϕ_i is a phase shift. The sum runs over different “shells” of neighbors, a shell being defined as a set of neighbors having the same distance from the emitter, R_i . In principle, the desired values for R can be extracted from χ by a Fourier transformation. Unfortunately the phase shift depends of the energy (through k). One can use calculated phase shifts or “experimental” phase shifts. The reason is that only the phase shift for 180° back scattering is of interest, not the phase shifts for all the other scattering angles. The 180° phase shift can be

obtained from a material which contains the scatterer of interest and has a known structure, e.g. a single crystal. The amplitude function for the different shells is given by:

$$A_i(k) = (N_i/R_i^2) \cdot |f_i(180^\circ, k)| \cdot W(T, K) \cdot \exp(-2R_i/\lambda)$$

N_i is the number of atoms in the shell. The $1/R^2$ factor leads to an effective localization of EXAFS explaining the success of a single-scattering treatment. It is caused by the fact that both emitter and scatterer are point sources. The next factor is the modulus of the scattering amplitude. $W(T, K)$ is a Debye-Waller factor which takes the thermal vibrations into account and the last factor describes the inelastic scattering of the electrons in the solid.

Example:

Ni K-edge EXAFS spectra (left) and their Fourier transform magnitudes (right) measured on the as deposited Ni/Al multilayer sample and on samples after ion mixing at substrate temperatures -140°C , 130°C , 230°C , 280°C and 330°C . For comparison the spectra of Ni metal and NiAl monocrystal are added. Solid line - experiment; dashed line - EXAFS model. Spectra recorded at the XAS13 experimental station of the DCI storage ring at LURE, Orsay (France).

